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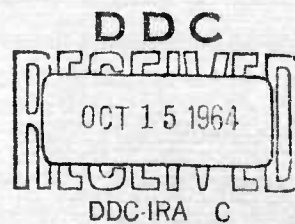
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ITRI



Report No. IITRI-C227-7 & 8  
(Technical Summary Report)

RESEARCH ON CHEMISTRY OF  $O_3F_2$  AND  $O_2F_2$

Air Force Office of Scientific Research  
Washington, D. C.

IIT RESEARCH INSTITUTE

Report No. IITRI-C227-7 & 8  
(Technical Summary Report)

RESEARCH ON CHEMISTRY OF  $O_3F_2$  AND  $O_2F_2$

January 1 through June 30, 1964

Contract No. AF 49(638)-1175  
IITRI Project C227

*ARPA*

Prepared by

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Air Force Office of Scientific Research  
Washington 25, D. C.

Copy No. 35

September 1, 1964

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## FOREWORD

This is Report No. IITRI-C227-7 and C227-8, Technical Summary Report No. 7 and 8, which covers the period from January 1 through June 30, 1964, on IITRI Project C227, Contract No. AF 49(638)-1175, entitled, "Research on Chemistry of  $O_3F_2$  and  $O_2F_2$ ."

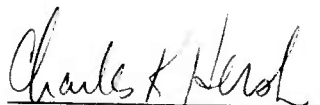
This research is being supported by the Advanced Research Projects Agency under ARPA Order No. 350-62, Project Code No. 9100. Technical Direction is being provided by the Director of Engineering Sciences, SREP, Air Force Office of Scientific Research.

In addition to the author, who is the principal investigator, personnel contributing to the program include: R. I. Brabets, Research Engineer; J. Keith, Research Chemist; R. Uenishi, Research Chemist; J. Finn, Associate Chemist; A. Kacmarek, Associate Chemist; J. Raney, Associate Physicist; R. Douthart, Assistant Chemist; G. Macur, Assistant Chemist; and W. Sumida, Assistant Chemist.

Respectfully submitted,

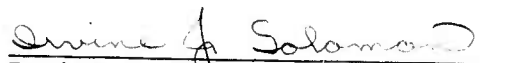
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## RESEARCH ON CHEMISTRY OF $O_3F_2$ AND $O_2F_2$

### I. INTRODUCTION

The following are the major objectives of this program:

- (1) the elucidation of the chemistry of  $O_3F_2$  and  $O_2F_2$  with inorganic compounds, (2) the study of the physical properties of  $O_4F_2$  as a means of revealing the presence or absence of ionic species in  $O_4F_2$ , (3) the determination of the oxidizing species remaining in solution after fluorination of nitric acid, and (4) the determination of the feasibility of preparing new ions of the type  $NF_4^+$  and  $NH_2F_2^+$ .

### II. RESULTS AND DISCUSSION

#### A. $NF_4^+$ , $N_2F_5^+$ , and $H_2NF_2^+$ Ions

The formation of ionic species such as  $NF_4^+$  and  $N_2F_5^+$  depends on several factors. For example, an important prerequisite for the formation of  $NF_4^+$  is certainly the availability of unshared electrons in the parent compound, another is the nature of the attacking electrophile. Probably the solvation of these ions is also an important factor. An answer to the question of whether these ions can exist must be based on a detailed study of these factors. This study is in progress, and the significant results which have been obtained are summarized below.

## 1. Difluoramine Additives

The reactions of difluoramine and methyl difluoramine with various acids are being studied in order to estimate the base strength of these amines. Although difluoramine is a very weak base, it does form compounds with strong acids such as  $\text{BF}_3$  and  $\text{PF}_5$ . In each of these systems, however, no useful thermodynamic data can be obtained which would enable us to quantitatively determine the base strength of the amine. In the vapor phase  $\text{HNF}_2\text{-BF}_3$  is too highly dissociated for the dissociation equilibrium to be examined, and irreversible decomposition occurs in the  $\text{HNF}_2\text{-PF}_5$  system.<sup>1</sup> Methyl difluoramine also forms compounds with these acids, but irreversible decomposition to  $\text{HCN}$ ,  $\text{HF}$ , etc. readily occurs.<sup>2</sup>

We have examined the behavior of difluoramine with several other acids, namely, hydrogen chloride, sulfur trioxide, trimethyl aluminum, and trimethyl gallium, and work on methyl difluoramine and these acids has been initiated.

### a. Hydrogen Chloride

A pressure composition study of the  $\text{HNF}_2\text{-HCl}$  system (from  $-138$  to  $-112^\circ\text{C}$ ) showed only positive deviations from Raoult's Law, indicating no interaction (Figure 1). Strong negative deviations were observed

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<sup>1</sup>Hercules Powder Co., Contract No. DA-31-124-ARO(D)-62, Quarterly Report No. 1, June 15, 1963.

<sup>2</sup>Ibid., Quarterly Report No. 3, December 16, 1963.

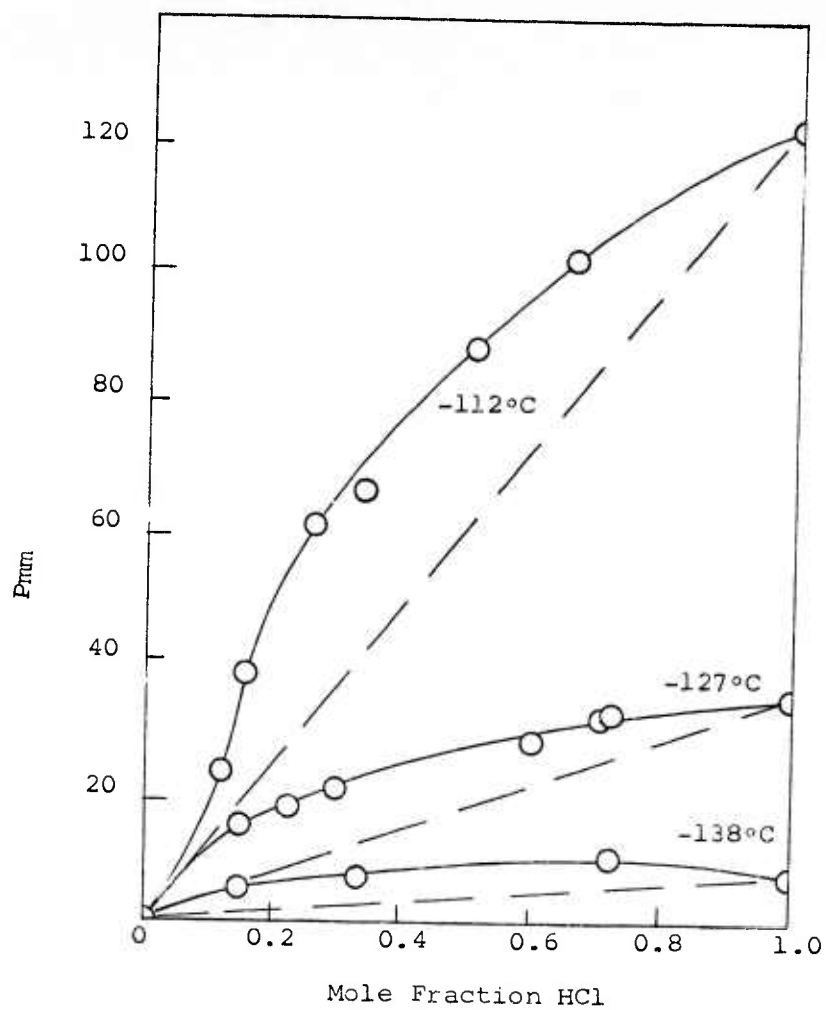


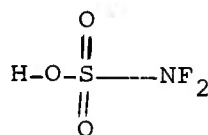
Figure 1  
THE HNF<sub>2</sub>-HCl SYSTEM

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with methyl difluoramine, and at  $-127^{\circ}\text{C}$ , the formation of a weak 1:1 additive was indicated (Figure 2). During the study of the compatibility of methyl difluoramine with mercury a sealed Pyrex tube containing these two components exploded violently while it was being shaken.

b. Sulfur Trioxide

It has been reported that  $\text{HNF}_2$  and  $\text{SO}_3$  form a 1:1 compound and possibly a 1:2 compound.<sup>3</sup> The pressure composition diagram shown in Figure 3 was obtained at  $0^{\circ}\text{C}$ . The proton and  $\text{F}^{19}$  NMR spectra show the structure to be

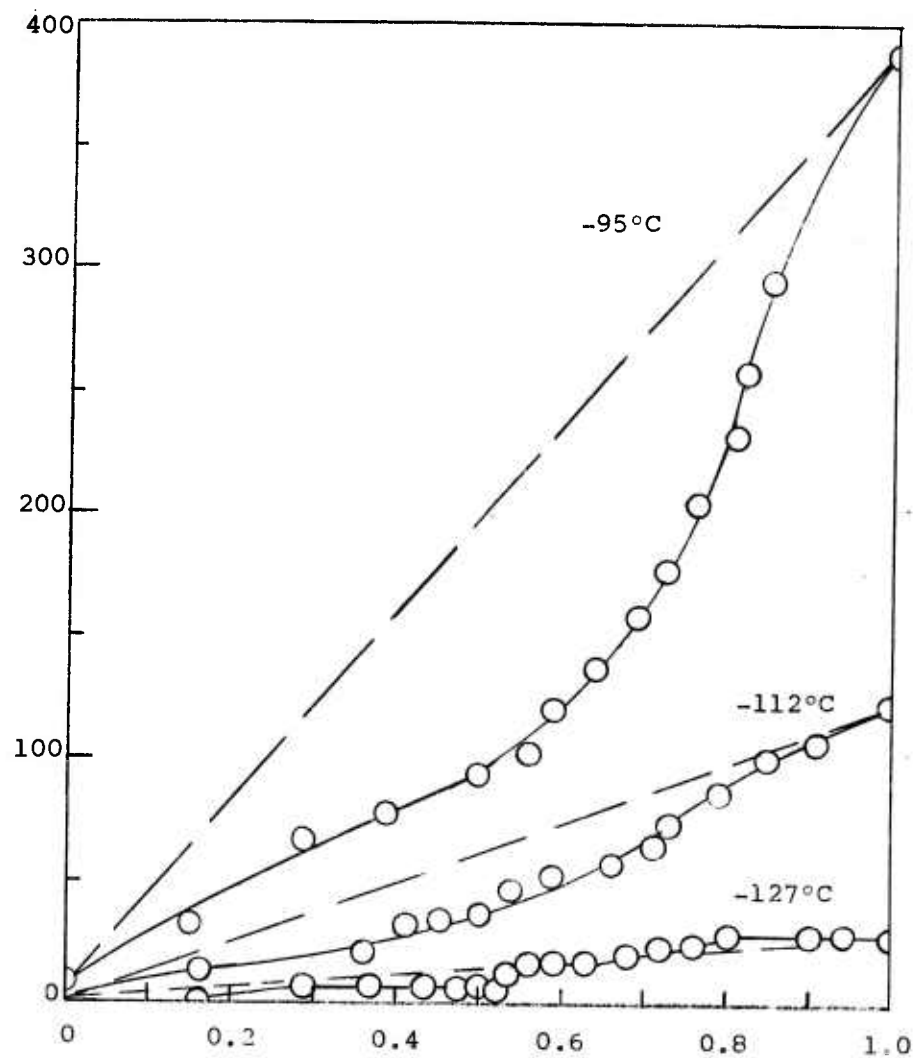


Slow decomposition occurs at room temperature, yielding  $\text{SO}_2$ ,  $\text{N}_2\text{F}_4$ , and presumably  $\text{H}_2\text{SO}_4$ .

c. Trimethyl Aluminum

Since a rather strong acid is required to form a stable complex with difluoramine, we investigated the reaction of difluoramine with trimethyl aluminum and trimethyl gallium. The reaction with trimethyl aluminum invariably resulted in explosion if the difluoramine

<sup>3</sup>Solomon, I.J., "(U) Research on Chemistry of  $\text{O}_3\text{F}_2$  and  $\text{O}_2\text{F}_2$ ," Yearly Summary Report No. IITRI-C227-6, IIT Research Institute Chicago, Ill., Feb. 1964.

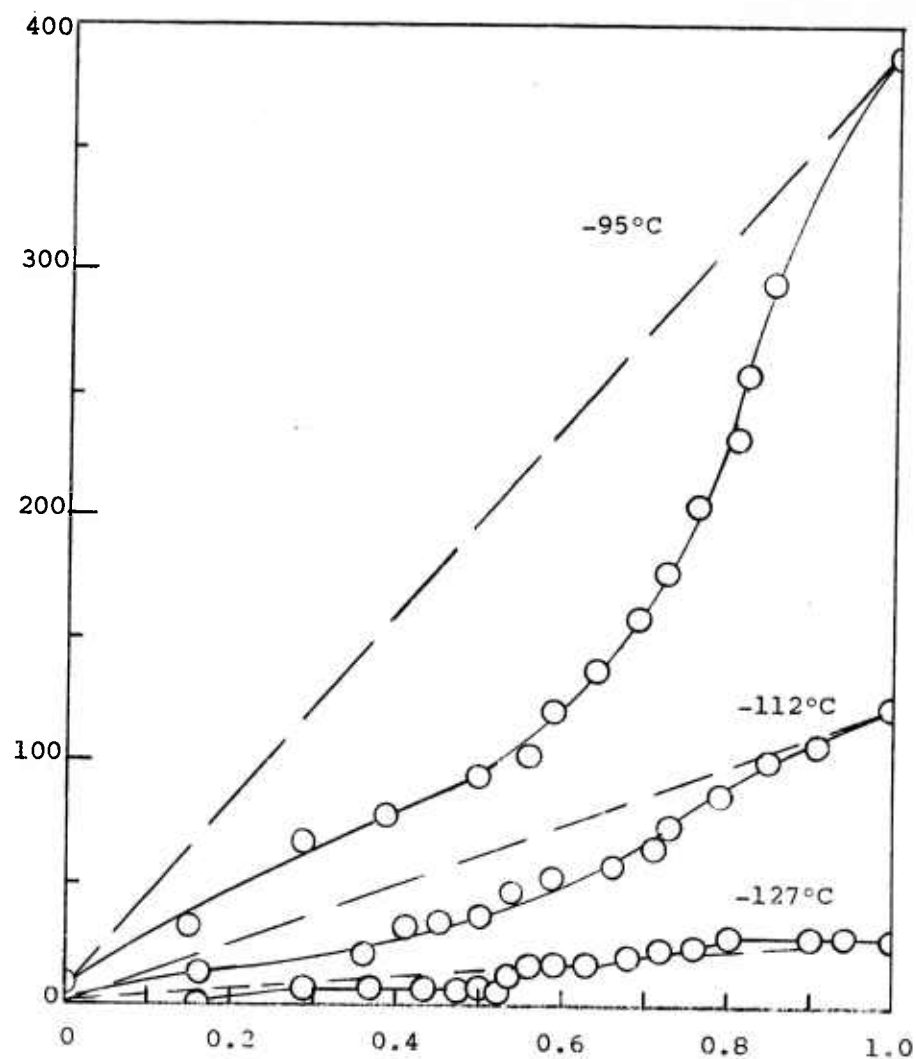


Mole Fraction HCl

Figure 2

THE  $\text{MeNF}_2$ -HCl SYSTEM

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Mole Fraction HCl

Figure 2

THE  $\text{MeNF}_2$ -HCl SYSTEM

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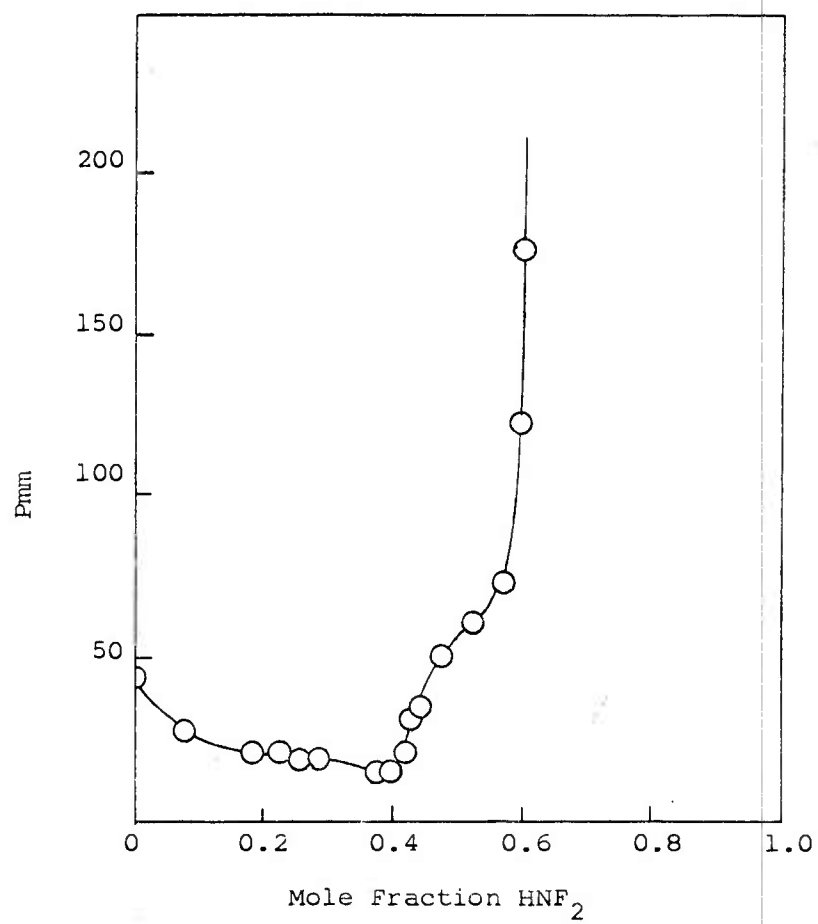
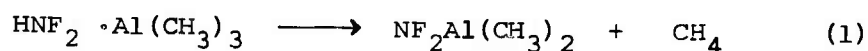


Figure 3  
THE  $\text{HNF}_2$ - $\text{SO}_3$  SYSTEM AT  $0^\circ\text{C}$

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was added too rapidly or the mixture warmed too rapidly. The reaction occurred slowly when difluoramine was added in small quantities at  $-80^{\circ}\text{C}$ , although slight decomposition occurred even under these conditions. Vapor pressure measurements could not be made because of irreversible decomposition, presumably according to Equation 1.



The decomposition product can react further with difluoramine. A sample of trimethyl aluminum was treated with an equivalent quantity of difluoramine and the adduct allowed to decompose according to Equation 1. A second equivalent of difluoramine was added, and the mixture slowly thawed. The mixture exploded with a bright green flash, although with less violence than a mixture of trimethyl aluminum and difluoramine. The mixture exploded with a bright green flash, although with less violence than a mixture of trimethyl aluminum and difluoramine. This system will be reexamined in an attempt to completely replace the methyl groups by  $\text{NF}_2$  groups, forming  $\text{Al}(\text{NF}_2)_3$ . To our knowledge  $\text{NF}_2\text{-Al}(\text{CH}_3)_2$  is the first example of an  $\text{Al-NF}_2$  bond, and the method can certainly open a route to interesting compounds containing more than one  $\text{Al-NF}_2$  bond.

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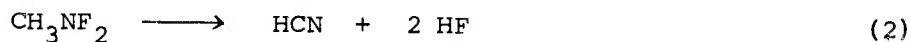
d. Trimethyl Gallium

Trimethyl gallium reacts slowly with difluoramine when the two are mixed and thawed. A viscous, colorless liquid is formed, and methane is slowly produced. The presence of excess difluoramine after two days, however, indicated that the reaction does not proceed beyond the formation of  $\text{F}_2\text{NGa}(\text{CH}_3)_2$ . This reaction is being studied further.

2. Methyl Difluoramine Additives

The additives of methyl difluoramine ( $\text{CH}_3\text{NF}_2$ ) with various Lewis acids are also being studied.

Equimolar quantities of trimethyl aluminum and methyl difluoramine were condensed in a glass tube, and the tube was sealed and thawed. At a temperature below  $0^\circ\text{C}$ , vigorous frothing was noted in the portion of the tube where the trimethyl aluminum condensed. A viscous liquid was present when the tube was examined at room temperature. After 4 days, a clear glassy solid was observed in the bottom of the tube. Two moles of methane and about  $1/3$  mole of HCN were the only volatile products. Heating of the residual solid produced a small amount of noncondensable material and a trace of sublimable solid, but all of the hydrogen cyanide could not be recovered. The reaction is presumably:



The missing hydrogen cyanide is probably complexed with  $\text{CH}_3\text{AlF}_2$ . This irreversible decomposition is consistent with the behavior of methyl difluoramine toward other acids such as  $\text{BF}_3$  and  $\text{PF}_5$ .

### 3. Dimethyl Fluoramine Additives

In order to complete this phase, the additives of dimethyl fluoramine,  $(\text{CH}_3)_2\text{NF}$ , with various Lewis acids are also being studied.

Synthesis of dimethyl fluoramine was accomplished by the dry fluorination of  $(\text{CH}_3)_2\text{NCOH}$ . A positive pressure flow of 90% dilution of  $\text{F}_2$  in He at  $0^\circ\text{C}$  resulted in a poor yield. By fluorinating the  $(\text{CH}_3)_2\text{NCOH}$  under a vacuum of 100 to 250 mm Hg pressure, the yield was noticeably improved. Since the infrared spectrum of dimethyl fluoramine was not found in the literature, the compound will be tentatively identified from the vapor pressure data, and confirmed by its mass-cracking pattern and its NMR spectrum.

Presently the difficulty lies in the isolation of the compounds fractionated in the vapor pressure range of dimethyl fluoramine. A recourse to the synthesis of dimethyl fluoramine was attempted by using N,N-dimethyl acetamide  $(\text{CH}_3)_2\text{NCOCH}_3$  instead of the formamide. A better yield is obtained by using the acetamide, but the problem of purifying the desired product is not easily accomplished by vacuum distillation. These products are currently being examined by gas chromatography.

B. Physical Properties of  $O_4F_2$

The nature of  $O_4F_2$  in both the vapor and the condensed phases is being studied in an attempt to answer the following questions: Does  $O_4F_2$  vaporize into  $(O_2F)_2$  and/or  $O_2F$ , or does it decompose completely to  $O_2$  and  $F_2$ ? Is  $O_4F_2$  dimerized or ionized in the liquid or solution phase? That is, do ions such as  $OF^+$  and  $O_3F^-$  exist?

A new Pyrex vessel for the synthesis and study of  $O_4F_2$  has been fabricated. The vessel is equipped with three electrodes. The electrode used mainly for the synthesis of  $O_4F_2$  extends into the center of the vessel. The other two electrodes, which are used for both synthesis and electrical measurements, are positioned on either side of the vessel. These two electrodes are shielded by small-diameter Pyrex tubing. Platinum wires lead from the shielded electrodes to the platinum rings of the capacitance cell, which is much smaller than the main vessel and consists of two small concentric platinum rings which were made from platinum sheets.

Future work will be devoted to the calibration of the capacitance cell and measurements of the capacitance of the cell containing pure liquid oxygen and later  $O_4F_2$ .

A measuring cell has a certain fixed capacitance,  $C_1$ , through the insulation of the platinum rings or cylinders from one another and between the electrodes. Neglecting the small deviation of the dielectric constant of air from unity, the capacitance when measured with air in the cell is therefore

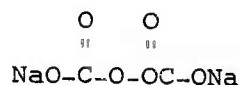
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$C_0 + C_1$  and, when measured with a liquid of dielectric constant  $\epsilon$  in it, is  $\epsilon C_0 + C_1$ . By using a pure liquid of known dielectric constant such as benzene,  $C_0$  and  $C_1$  can be determined and used for the measurement of the dielectric constant of an unknown material. Capacitance measurements of the cell containing liquid oxygen will also be made. Since  $O_4F_2$  contains more than 61% oxygen, it will be of considerable interest to compare measurements of both liquid oxygen and  $O_4F_2$ . Liquid oxygen is reported to have a dielectric constant of about 1.46 at  $-182^\circ C$ .

#### C. Reactions of $O_2F_2$

##### 1. Disodiumperoxydicarbonate

A study leading to the possible synthesis of polyoxyfluoride compounds was continued on a limited basis. The fluorination of disodiumperoxydicarbonate



was investigated by using  $O_2F_2$  as the fluorinating agent. As a comparison, static fluorination with pure  $F_2$  gas and  $CsF$  catalyst was employed as a more drastic means of fluorinating at low temperatures. This study was continued from a previous experiment in which  $OF_2$  was the principal product of a  $-78^\circ C$  reaction in a 25%  $F_2$ -He gas mixture by using a fluidizing bed technique of fluorination. At high temperatures (above  $0^\circ C$ ),  $CO_2$ , usually the principal product, resulted from the decomposition of the peroxydicarbonate. The purpose of the various means of fluorination

was to examine their fluorinating efficiency as well as the feasibility of low-temperature reactions in order to counter the instability problem of the peroxydicarbonate experienced at higher temperatures.

Two preliminary runs were conducted by reacting  $O_2F_2$  with (70% pure) disodiumperoxydicarbonate. The first experiment was conducted in a manner similar to a previous experiment (Report No. IITRI-C227-6) in which an implosion (or explosion) had occurred. The liquid  $O_2F_2$  was left in contact with the peroxydicarbonate, and the reaction system continuously pumped. During 1 hr at  $-160^\circ C$ , no perceptible products collected in the  $-196^\circ C$  trap downstream from the reactor. At  $-111^\circ C$ , liquid  $O_2F_2$  completely disappeared from the reactor after several minutes. An infrared analysis of the total condensed products indicated the presence of  $CO_2$ ,  $COF_2$ ,  $CF_4$ , and other unidentified compounds.

For the second run, a Helicoid vacuum gage was attached to the reactor system to measure pressure changes during the reaction. At  $-160^\circ C$ , a small pressure change was observed when  $O_2F_2$  was left in contact with excess  $Na_2C_2O_6$  for a 3-hr period. Analyses of the noncondensable gases resulted in recovery of trivial amounts of  $O_2$  and  $F_2$  gases at this temperature. Further contact of liquid  $O_2F_2$  with  $Na_2C_2O_6$  was conducted at  $-111^\circ C$  for 6 hr. The  $O_2F_2$  completely decomposed or reacted in this experiment. The amount of  $O_2$  recovered was about three times that of  $F_2$ .  $CO_2$  comprised a major portion of the total amount

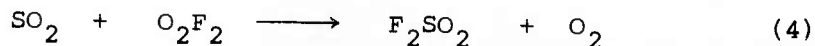
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of condensible products, and  $\text{COF}_2$ ,  $\text{SiF}_4$ , and other unidentified constituents comprised the remaining portion. Warming to room temperature yielded only  $\text{CO}_2$  and  $\text{O}_2$ , the decomposition products of the peroxydicarbonates. From these experimental results  $\text{O}_2\text{F}_2$  does not appear to be a suitable fluorinating agent for the peroxydicarbonate, and work on this approach was concluded.

In the static fluorination experiment, one atmosphere of pure  $\text{F}_2$  gas at  $-183^\circ\text{C}$  was kept in contact with a mixture of  $\text{Na}_2\text{C}_2\text{O}_6$  and excess  $\text{CsF}$  for one week. The reactant-catalyst system was contained in a portable Pyrex storage bulb. The noncondensable gases pumped out of the bulb at  $-196^\circ\text{C}$  appear to be entirely fluorine, and infrared spectral analysis of the small amount of condensible products indicated the presence of  $\text{COF}_2$ ,  $\text{SiF}_4$ ,  $\text{CO}_2$ , and other unidentified compounds. No other product was recovered when the storage bulb was warmed to  $-78^\circ\text{C}$ . Above this temperature, the decomposition products of the starting material,  $\text{CO}_2$  and  $\text{O}_2$ , are expected. Thus, only a slight reaction takes place at  $-183^\circ\text{C}$ .

## 2. Sulfur Oxides and Oxyfluorides

Sulfur dioxide reacted vigorously with  $\text{O}_2\text{F}_2$ , producing a variety of interesting products; however, the main reaction is:



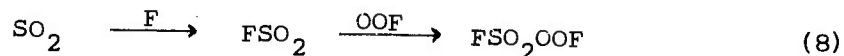
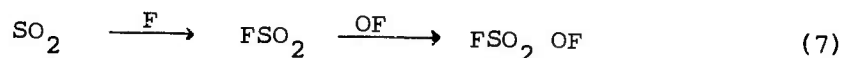
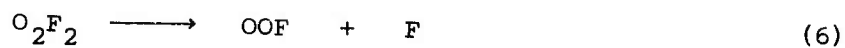
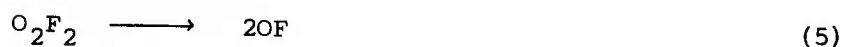
In a typical reaction 15.6 mmoles of sulfur dioxide was allowed to react with 15.5 mmoles of  $\text{O}_2\text{F}_2$  at  $-160^\circ\text{C}$  in the absence of a solvent. The reaction products were passed through liquid nitrogen traps and a sodium chloride tube, and the remaining noncondensable

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gas ( $O_2$ ) was transferred by means of a Toeppler pump and measured. The condensible gas was then further fractionated. The amounts of the various products are listed below:

$F_2$	1.9 mmoles
$F_2S_2O_5$	1.2 mmoles
$F_2S_2O_5, SO_2$	1.4 mmoles
$FSO_2 OF, FSO_2 OOF$	1.4 mmoles
$F_2SO_2$	10.3 mmoles
$O_2$	11.0 mmoles

Thus, as noted previously, the main reaction is represented by Equation 4 in addition to other side reactions. The side reactions are the most interesting in that OF- and OOF-containing materials are formed. This is especially so since the products  $FSO_2OF$  and  $FSO_2OOF$  involve the addition of OF and OOF, respectively, to  $SO_2$ . The reaction may perhaps be represented as:

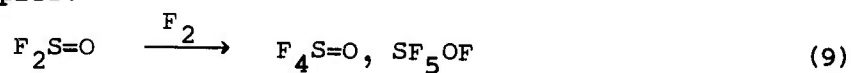



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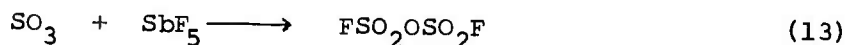
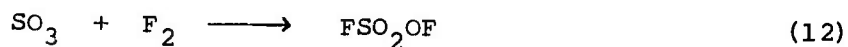
<sup>4</sup>F.B. Dudley, G.H. Cady and D.F. Eggers, Jr., J. Am. Chem. Soc. 78 29 (1956).



The product of Equation 7 was previously reported by Cady and co-workers, but only by the fluorination of  $\text{SO}_3$ . In all previous work in which sulfur oxides or oxyfluorides were fluorinated it has not been possible to obtain products containing more S-O bonds than in the reactant. That is, S-O bonds are not formed by any dispersion reactions. The following reactions are given as examples:



Fluorine fluorosulfonate ( $\text{FSO}_2\text{OF}$ ) and pyrosulfuryl fluoride ( $\text{FSO}_2\text{OSO}_2\text{F}$ ) were previously prepared from  $\text{SO}_3$ .



It is not surprising that  $\text{F}_2\text{SO}_2$  is the main product in the reaction of  $\text{SO}_2$  with  $\text{O}_2\text{F}_2$ , since it results from a simple fluorination of  $\text{SO}_2$ . Also, it was found in an independent experiment that  $\text{F}_2\text{SO}_2$  does not react further with  $\text{O}_2\text{F}_2$ . Also,  $\text{F}_4\text{SO}$  does not react with  $\text{O}_2\text{F}_2$ .



Also,  $\text{S}_2\text{O}_5\text{F}_2$  is formed from  $\text{SO}_2$  and  $\text{FSO}_2\text{OF}$ , and therefore it may be formed in one of two ways.

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Another interesting fact was found in these experiments, that is,  $O_2F_2$  is more soluble in  $F_2SO_2$  and  $F_4SO$  than in Freon 13, the solvent currently thought of as the best for  $O_2F_2$ . Some decomposition rates were determined in the solvents in order to ascertain the usefulness of these solvents for future studies. The results are given in Table 1.  $O_2F_2$  decomposes at a slightly higher rate in  $F_2SO_2$  and  $F_4SO$  than in Freon 13, but the decomposition rates are slow enough in any of these so that they can be used as solvents.

Table 1

DECOMPOSITION RATES OF  $O_2F_2$  IN VARIOUS SOLVENTS

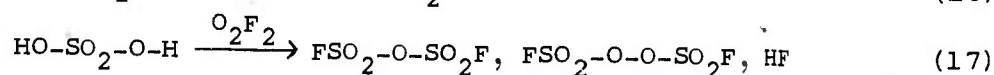
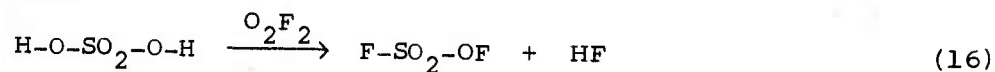
Temp, °C	Decomposition Rates, % per hr		
	$F_2SO_2$	$F_4SO$	Freon 13
-139	0.022	0.25	0.20
-112	0.22	1.02	0.20
-95	1.39	1.50	1.57

It was thought that  $F_2SO_2$  and  $F_4SO$  might also be solvents for  $O_2BF_4$ . However, two preliminary experiments showed no solution of  $O_2BF_4$  in these solvents.

The reactions of  $H_2SO_4$  and  $H_2SO_5$  with  $O_2F_2$  were also studied. Sulfuric acid reacts very slowly; the reaction of 3 mmoles of  $H_2SO_4$  and 3 mmoles of  $O_2F_2$  at  $-130^\circ C$  yielded only 0.23 mmoles of product. This product was  $FSO_2OF$ ,  $F_2S_2O_5$ ,  $F_2S_2O_6$ ,

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and  $\text{SiF}_4$ . These are the expected products from the following reactions in which various bonds are fluorinated.



The rate of reaction of  $\text{H}_2\text{SO}_5$  with  $\text{O}_2\text{F}_2$  was faster than with  $\text{H}_2\text{SO}_4$ ; that is, 13 mmoles of  $\text{H}_2\text{SO}_5$  reacted with 21 mmoles of  $\text{O}_2\text{F}_2$  at  $-130^\circ\text{C}$  to produce about 5 mmoles of products. The main products were  $\text{FSO}_2\text{OF}$  and  $\text{SiF}_4$ ; small amounts of  $\text{F}_2\text{SO}_5$  and  $\text{F}_2\text{SO}_6$  were detected. These are the expected products.

In a few preliminary experiments  $\text{SO}_3$  was allowed to react with  $\text{O}_2\text{F}_2$ . It should be remembered that previous to this work  $\text{SOF}$  compounds were prepared only from compounds containing three  $\text{S-O}$  bonds. The reaction of  $\text{SO}_3$  with  $\text{O}_2\text{F}_2$  is so vigorous that the first attempt at studying this reaction resulted in an explosion. Subsequent reactions were run in  $\text{F}_2\text{SO}_2$  solvent. Some very interesting results were obtained. When 7.1 mmoles of  $\text{SO}_3$  and 8.0 mmoles of  $\text{O}_2\text{F}_2$  were allowed to react in  $\text{F}_2\text{SO}_2$ , a large amount of product was obtained; however, when the product was warmed to room temperature,  $\text{O}_2$  (6.3 mmoles) and  $\text{F}_2$  (4.9 mmoles) were released. The only product that decomposed on warming will be further characterized.

D. Chemistry of  $O_3F_2$

In this phase of the program  $O_3F_2$  will be reacted with a number of inorganic compounds. In other words most of the work completed on the reactions of  $O_2F_2$  will be repeated by using  $O_3F_2$ . It must be remembered that the  $O_2F_2$  used in these experiments will always contain at least small amounts of  $O_3F_2$ . However, contrary to earlier work, it has been found that  $O_3F_2$  can be distilled if done with care.

The liquid nitrogen bath surrounding the U-trap containing the  $O_3F_2$  is dropped very slowly, preferably by evaporation of the liquid nitrogen. The  $O_3F_2$  is distilled through as short distance as physically possible and caught in an adjacent trap. The system is pumped during the entire operation. Some decomposition does result, but if liquid oxygen is used as the refrigerant, an extra bonus is obtained. The  $O_3F_2$  has a lower melting point than  $O_2F_2$  and will drain to the bottom and contact the sample under investigation, while the  $O_2F_2$  freezes out at the top of the tube.

The following materials have been investigated with  $O_3F_2$ : calcium, magnesium, potassium, sodium, lithium, sodium fluoride, sodium bromide, sodium iodide, sodium nitrite, and sodium nitrate.

Calcium and magnesium do not react at all. The alkali metals react smoothly. The sodium halides react as expected: NaBr - some reaction to liberate bromine; NaI - appreciable reaction to liberate iodine. Sodium nitrite and nitrate do not

seem to give appreciable reactions. Now that the preliminary reactions have been carried out, some of the more interesting results will be studied during the next quarter.

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